Supplementary Information: Environmental electrometry with luminescent carbon nanotubes

Jonathan C. Noé,¹ Manuel Nutz,¹ Jonathan Reschauer,¹ Nicolas Morell,² Ioannis Tsioutsios,² Antoine Reserbat-Plantey,² Kenji Watanabe,³ Takashi Taniguchi,³ Adrian Bachtold,² and Alexander Högele¹

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¹Fakultät für Physik, Munich Quantum Center, and Center for NanoScience (CeNS),

Ludwig-Maximilians-Universität München, Geschwister-Scholl-Platz 1, 80539 München, Germany

²ICFO-Institute de Ciencies Fotoniques, The Barcelona Institute of Science and Technology, 08860 Castelldefels Barcelona, Spain

³National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

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I. EXPERIMENTAL METHODS

A. Sample preparation

Hexagonal boron nitride (hBN) was exfoliated on p-doped silicon substrate with a thermal silicon oxide (SiO₂) layer of 285 nm. The mechanical exfoliation was performed using a standard clean-room adhesive scotch tape technique yielding thin hBN patches (typically $10 - 700 \ \mu m^2$) on SiO₂. Carbon nanotubes (CNTs) were grown subsequently by chemical vapor deposition (CVD). To this end, a diluted catalyst suspension consisting of iron nano-particles grafted on aluminum oxide particles dissolved in methanol was drop-casted on the substrate with a homogeneous distribution over the SiO₂ surface and hBN flakes. The sample was baked at 150 °C for 10 minutes and placed in a quartz tube furnace, which was subsequently heated up under a flux of hydrogen (400 sccm) and argon (500 sccm). At 900 °C, methane gas was injected at a flux of 550 sccm to initiate the growth of CNTs for 10 minutes. The resulting sample with CNTs on SiO₂ and hBN was characterized by Raman spectroscopy and atomic force microscopy (AFM).

B. Photoluminescence microscopy and spectroscopy

Photoluminescence (PL) experiments were performed in a home-built cryogenic confocal microscope. The sample was positioned with piezo-stepping and scanning nano-positioners (*attocube systems* ANPxyz101 and ANSxy100) into the confocal excitation and detection spots of a low-temperature apochromatic objective (*attocube systems* LT-APO/NIR/075) with a diffraction limited spot of $\sim 1 \mu m$. The microscope unit with the objective and the sample was placed in a dewar with an inert helium atmosphere at a pressure of 20 mbar and immersed in a liquid helium bath cryostat with the base temperature of 4.2 K. Excitation around 790 - 850 nm was performed with a wavelength-tunable Ti:sapphire laser system (*Coherent* Mira) in continuous wave mode at $10 - 50 \mu W$ excitation power. The PL was spectrally dispersed by a monochromator (*Roper Scientific* Acton SP 2750) and recorded with a nitrogen-cooled silicon CCD (*Roper Scientific* Spec 10:100BR/LN) with integration times in the range of 1 - 30 s.

II. THEORETICAL MODELLING AND SIMULATIONS

A. Allan deviation

To quantify the spectral stability of the CNT PL we used the Allan deviation s_e calculated as [1]:

$$s_e = \sqrt{\frac{1}{2} \cdot \frac{1}{N-1} \cdot \sum_{n=1}^{N-1} (e_n - e_{n+1})^2},$$
(1)

where e_n is the PL peak energy of the *n*-th consecutive spectrum out of the total number of spectra *N*. Analogous to the standard deviation, the Allan deviation quantifies the magnitude of spectral fluctuations. In contrast to the standard deviation, however, its time evolution does not depend on the exponent α for spectral fluctuations characterized by a power law $1/f^{\alpha}$ [1] and is therefore used to analyze the PL fluctuations of the CNTs in our study exhibiting varying α in their noise spectral density.

B. Model of the dipolar carbon nanotube electrometer

Spectral fluctuations in the CNT PL are modeled in the framework of electrostatic interactions between the permanent electric dipole moment of a localized CNT exciton and fluctuating charge traps on the surface of the underlying substrate (Fig. S1a). The localized exciton with a permanent dipole moment \mathbf{p} (indicated by the light blue arrow) is placed at the origin of the coordinate system at the apex of the CNT with diameter d_{CNT} residing in vacuum on a substrate with the dielectric constant ϵ_r . The charge trap is modeled by an electron with the elementary charge -e on the substrate surface and the corresponding mirror charge e within the substrate at distance vectors \mathbf{r} and \mathbf{r}_m (along the corresponding unit vectors $\hat{\mathbf{r}}$ and $\hat{\mathbf{r}}_m$) from the CNT exciton dipole, respectively. The dipolar field of the charge trap (grey lines) induces a shift in the PL energy of the localized exciton via the first-order Stark effect according to:

$$\Delta E_{\rm PL} = \frac{-e}{4\pi\epsilon_0} \mathbf{p} \cdot \left(\frac{\mathbf{\hat{r}}}{|\mathbf{r}|^2} - \frac{1-\epsilon_r}{1+\epsilon_r} \cdot \frac{\mathbf{\hat{r}}_m}{|\mathbf{r}_m|^2} \right)$$
(2)

with the vacuum permittivity ϵ_0 . We use $d_{CNT} = 0.7$ nm as a typical value for the CNTs of our study and $\mathbf{p} = (0.35, 0, 0.27)$ eÅ [2] as an estimate of the electric dipole moment of excitons localized by unintentional disorder in our cryogenic CNTs. Different orientation, position and magnitude of the exciton dipole moment do not change the qualitative results of the simulations.



FIG. S1: (a) Model schematics: The localized exciton with a permanent dipole moment **p** (light blue arrow) resides in vacuum at the apex of the CNT on a substrate with the dielectric constant ϵ_r . A nearby charge trap is modeled by an electron that creates along with its mirror charge a dipolar field at the location of the exciton thus giving rise to a spectral shift in the exciton photoluminescence. (b) Model parameters: N trap states (grey crosses) with average lifetime τ are distributed randomly in a circle (grey) with radius r_{max} around the nanotube. A region free of charge traps around the carbon nanotube can be ensured by an exclusion circle (pink shaded area) with radius r_{min} .

With this geometry, we used Monte Carlo simulations to determine the characteristic spectral power density of CNTs with temporal PL fluctuations arising from charging and discharging events in the nearby traps. To this end, as shown schematically in Fig. S1b, N trap states 0.1 Å above the dielectric substrate (grey crosses) with a characteristic trapping and release time τ were considered in a random distribution around the CNTs within a circle of radius r_{max} which provides a cut-off to the simulations by defining a maximum sensitivity distance to a single trap. At r_{max} (with different values of 37 nm and 44 nm for charge traps on hBN and SiO₂, respectively, due to different dielectric constants), the field amplitude of a charge dipole decays to $1/e^2$ of the value that would result in a PL energy shift equal to the spectral resolution limit of our spectrometer ($\sim 0.1 \text{ meV}$). Where required, an exclusion circle with a finite radius r_{\min} can be used to impose an area free of charge traps around the CNT.

For each simulation run N trap states were distributed randomly within r_{max} with a subsequent removal of traps inside of r_{min} . The initial state of every trap (either occupied by an electron or empty) was chosen randomly. The capture and release of electrons on the characteristic time scale τ leads to a time-dependent effective electric field at the position of the CNT which in turn give rise to spectral shifts of the exciton PL peak frequency ω_0 . The time evolution $\omega_0(t)$ with frequency resolution determined by our spectrometer was sampled 1000 times with a time bin $t_{\text{bin}} = 1$ s (corresponding to a rate $1/t_{\text{bin}}$ of 1 Hz), resulting in a total temporal evolution time T = 1000 s. The noise spectral density S(f) was then obtained within the bandwidth ranging from 1/T to $1/(2t_{\text{bin}})$ for discrete frequencies f = k/T (with integer number k and $k_{\text{max}} = T/2t_{\text{bin}}$) from the ratio of $\omega_0(t)$ and its time average $\langle \omega_0(t) \rangle$ by Fast Fourier Transform (FFT) [3]:

$$S(f) = |\text{FFT}[\omega_0(t)/\langle\omega_0(t)\rangle]|^2 (t_{\text{bin}})^2/T,$$
(3)

and normalized such that total noise spectral density equals unity:

$$\sum_{k=1}^{k_{\text{max}}} S(k/T) = 1 \text{ Hz}^{-1}.$$
(4)

Subsequently, the normalized noise spectral density was decomposed into individual components of random telegraph noise $S_t(f)$, pink noise $S_p(f) = pf^{-1}$, and frequency-independent white noise S_w as in Eq. 1 of the main text:

$$S(f) = a \cdot S_t(f) + b \cdot S_p(f) + c \cdot S_w, \tag{5}$$

with the respective weights a, b and c ranging between 0 and 1, and a + b + c = 1. The first term in the decomposition represents the random telegraph noise (RTN) component given by:

$$S_t(f) = n \frac{2(\Delta E)^2 \bar{\tau}}{4 + (2\pi f \bar{\tau})^2},$$
(6)

where ΔE is the energy difference between the two binary states of the CNT PL energy that correspond to charged and discharged trap states with a characteristic average switching time $\bar{\tau}$. The proportionality constant n follows from the normalization of $S_t(f)$ according to Eq. 4 with a = 1. The second term corresponds to the pink noise component with a proportionality factor $p = 1.47 \cdot 10^{-4}$ obtained from normalization of $S_p(f)$ according to Eq. 4 with b = 1, and the third term represents the white noise component with $S_w = 2 \cdot 10^{-3} \text{ Hz}^{-1}$ obtained from Eq. 4 with c = 1.

The simulations were performed 100 times for each set of parameters. The main results are shown in Fig. S2. For the most simple case of a single fluctuating trap, S(f) should exhibit RTN only. Simulations of a rather stable dielectric environment characterized by a surface state density of $\sigma = 1 \cdot 10^{11}$ cm⁻² (an order of magnitude lower than in SiO₂) and long characteristic dwell times of charge states ($\tau > 100$ s) capture this limit by the dark blue data points in Fig. S2a. This limit is contrasted by using the parameters expected for SiO₂ (orange data points in Fig. S2 b) with $\sigma = 1 \cdot 10^{12}$ cm⁻² [4] and typical fluctuation



FIG. S2: Simulation results for different sets of parameters (density of surface trap states σ , their corresponding lifetime τ and minimum distance from the carbon nanotube r_{\min}). (a) Substrate with low spatial density of slowly fluctuating charge traps: $\sigma = 1 \cdot 10^{11} \text{ cm}^{-2}$, $\tau > 100 \text{ s}$, $r_{\min} = 0$ nm; all data points are concentrated at the lower left corner of the ternary diagram and are therefore barely distinguishable. (b) Parameters characteristic of SiO₂ representing the scenario of a high density of fast fluctuating surface states: $\sigma = 1 \cdot 10^{12} \text{ cm}^{-2}$, $\tau \le 3 \text{ s}$, $r_{\min} = 0$ nm. (c) A distant chain of charge fluctuators with high areal density which is likely to occur near hBN crystal ridges: $\sigma = 1 \cdot 10^{13} \text{ cm}^{-2}$, $20 \text{ s} < \tau < 60 \text{ s}$, $r_{\min} = 34 \text{ nm}$.

timescales of $\tau \leq 3$ s in accord with the actual observation of switching events as in the upper and right panels of Fig. 3a and Fig. 4a in the main text, respectively. The large white noise component is introduced by switching rates near and below the resolution limit of the FFT of 0.5 Hz given by $0.5/t_{\rm bin}$. The occurrence of 1/f noise is found to be related to distant accumulations of charge traps in an otherwise stable dielectric environment (Fig. S2 c) with $r_{\rm min}$ of at least ~ 30 nm, intermediate fluctuation times $20 \text{ s} < \tau < 60 \text{ s}$, and a high surface state density $\sigma = 1 \cdot 10^{13} \text{ cm}^{-2}$. The $1/r^2$ dependence of the dipole field results in a strong RTN contribution for all parameter sets (note the different scales of the ternary diagram) because there is always one nearest dominant trap state.

III. RELATION BETWEEN TOPOGRAPHY AND NOISE CHARACTERISTICS FOR NANOTUBES ON HEXAGONAL BORON NITRIDE

Our simulations suggest that a distant accumulation of fluctuation sites in an otherwise electrostatically passive environment is the origin of 1/f noise observed in the time evolution of the PL energy of localized CNT excitons on hBN. A possible realization of such a scenario is a chain of high density surface states at crystal ridges due to dangling bonds and accumulation of catalyst particles. This assumption is supported by complementary studies of local environments of CNTs on an hBN flake with atomic force microscopy (AFM) as in Fig. S3a, b and Kelvin probe force measurements (KPFM) as in Fig. S3e, f. Both AFM and KPFM imaging of a representative hBN flake of the sample (Fig. S3a, c, e, and f) reveal catalyst particles distributed randomly over hBN terraces as well as dense lines of particles agglomerated in chains along the crystal ridges. CVD-grown CNTs with sub-nanometer diameters (indicated by the arrows in Fig. S3b and d) identified on atomically flat hBN terraces (according to the ~0.4 nm steps in the height profile in Fig. S3c) in the vicinity of such chains of disorder (lines of high contrast in Fig. S3a, b, e, and f) visualize the scenario of CNTs with an increased 1/f noise component in the noise spectral density of the PL dynamics.



FIG. S3: Atomic force micrographs (a, b) and corresponding Kelvin probe force profiles (e, f) of a representative sample region with nanotubes on an hBN flake. Zooms to the regions indicated by the white squares in (a) and (e) are shown in (b) and (f). (c) and (d) Height profiles along the grey lines in (a) and (b), respectively. Data in (a), (c) and (e) identify atomically flat crystal terraces with randomly distributed catalyst particles as well as particle agglomerates along terrace ridges. Data in (b) and (d) show two carbon nanotubes (indicated by the arrows) with sub-nanometer diameters in the vicinity of such a terrace ridge with a chain of disorder. In (f) the lower nanotube is missing in the corresponding Kelvin probe force measurement).

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